

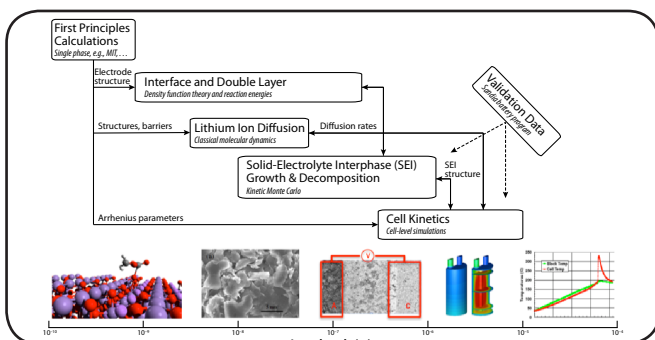
Mechanistic Multiscale Modeling of Battery Electrochemical Reactions

Sandia is developing numerical simulation capabilities to model and understand electrochemical mechanisms that lead to performance degradation, suboptimal reliability, and potential safety concerns in batteries. Our methodology is rooted in a first-principles description of electrode–electrolyte interface atomistic processes.

Transitioning from fossil-fueled to electrified vehicles depends on developing increasingly economical, reliable, and safe batteries. To substantially improve battery reliability and safety, we strive to increase understanding of the complex processes that can lead to performance degradation and thermal runaway through multiscale mechanistic modeling.

Why Mechanistic Modeling?

The energy storage community is working to improve battery cost, reliability, lifetime, and energy density. Simultaneously meeting these goals can potentially involve radically different electrochemical designs. Sandia is working to develop simulation tools to help understand the reliability and safety margins in the presence of these radical changes. Such tools require a complete understanding of the processes that lead to performance degradation, thermal abuse, and runaway for different battery chemistries—from the fundamental processes that are involved in electrolyte decomposition to the large-scale processes involved in electrode passivation and electrolyte transport and response.



Inputs and outputs to the Sandia Battery Abuse Modeling program, focus-ing on bridging the gap between atomistic and cell-level simulations. Each link in the chain builds on the results from the previous, finer-detail stage to ultimately deliver an accurate predictive capability that can assess new battery chemistries before building prototypes.

Sandia’s aim in mechanistic modeling is to understand the atomistic processes that lead to battery performance and safety issues in sufficient detail to reliably predict the behavior of new chemistries. This development will constitute a unique capability with far-reaching value for Sandia’s work in battery technology and energy systems for government sponsors and industry partners.

Multiscale Modeling of Thermal Runaway Onset

Predicting conditions that lead to thermal runaway conditions in a battery requires accurately modeling chemical reactions that release heat. This approach involves accurate, quantum-mechanical methods to track atomistic chemical reaction processes. These atomistic processes are coupled to processes that occur at longer length scales, such as the formation and stability of the solid–electrolyte interface (SEI) layer. This SEI, which provides a passivating layer on electrode surfaces, comprises a microstructure that is tens of nanometers long, and, thus, is too large to capture with even the fastest quantum techniques on the largest computers.

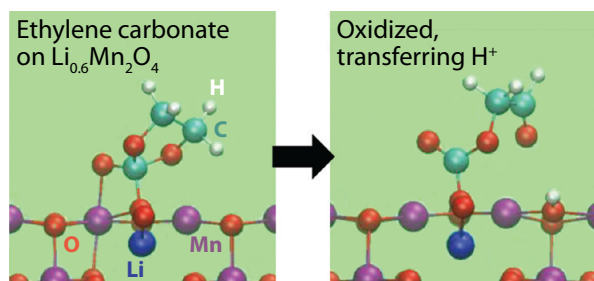
Sandia has thus developed a multiscale technique where we simulate the electrode (and a small portion of the electrolyte) in the field of the electrolyte using density functional theory, and then use a statistical fluids simulation approach to simulate the electrolyte in the field of the electrode. By iterating these two methods to self-consistency, we arrive at an approach that allows us to use the high-accuracy methods to simulate bond-breaking reactions, while still preserving an accurate description of the bulk response of the dielectric electrolyte. By using mesoscale techniques, including kinetic Monte Carlo

and phase-field approaches, the Sandia team captures the microstructural implications of the elementary reactions involved in decomposing electrolyte and forming the SEI passivation layer. These detailed mechanistic studies enable an understanding of when and how SEI-layer breakdown can promote rapidly accelerating chemical reactions—the onset of thermal runaway.

Modeling the SEI Layer and Its Chemical Reactions

That lithium-ion batteries lose their high power capacity over multiple cycles is a major technical barrier—a power fade related to electrolyte decomposition products formed on a battery’s solid surfaces, the SEI layer.

Another Sandia energy storage simulation effort seeks to develop a first-principles SEI model and to understand the chemical reactions that lead to its formation. Here, we study anode surface degradation (passivation layer formation), the chemical reactions in the liquid electrolyte, and cathode oxidation. These liquid–solid interface models explore chemical reactions at the 15–30 Å length scale and exploit Sandia’s world-class high-performance computation platforms to understand fast, kinetic-controlled reactions. A recent paper proposed a mechanism whereby cathode oxidation contributes to electrolyte decomposition in a way that may release transition metal ions which degrade the passivating SEI on the anode.



Ethylene carbonate (EC) is a key component of the electrolyte used in lithium-ion batteries. The Sandia team is investigating the initial EC decomposition steps on spinel $\text{Li}_{0.6}\text{Mn}_2\text{O}_4$ surfaces. They predict a slightly exothermic EC bond-breaking event on this oxide facet, which facilitates subsequent EC oxidation and proton transfer to the oxide surface. Both the proton and the partially decomposed EC fragment weaken the Mn–O ionic bonding network.

Complementary Simulation and Experiment

Sandia’s BATLab is a leading facility for investigating and understanding battery failure. Our goal is to develop a complementary modeling capability to help understand the mechanisms behind battery degradation and failure and to provide a predictive capability that can assess new battery chemistries in advance of their experimental realization.

Sandia mechanistic modeling teams work closely with experimentalists to confirm hypotheses and develop validation data where the models exhibit unacceptably large degrees of uncertainty. Given the current limitations of even the best high-performance computing, Sandia research teams explore idealized conditions. Looking at these isolated reaction examples can reveal mechanisms that would be hidden by experimental complexity, which can also lead to more precise experimental design. In addition, Sandia is building up a library of knowledge to use at the next stage in the multiscale modeling chain to build a complex picture that approximates real conditions—in which the energy storage community can have some measurable degree of confidence.

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